

## **AMENDMENTS TO THE CLAIMS**

### **Listing of Claims**

1. (currently amended) A photocatalytically-activated self-cleaning article of manufacture comprising:

a substrate having at least one surface; and

a photocatalytically-activated self-cleaning coating comprising a combination of anatase phase and amorphous phase of titanium dioxide deposited over the surface of the substrate at a thickness of less than 1,000 Angstroms by a process selected from the group consisting of chemical vapor deposition, magnetron sputtered vacuum deposition and spray pyrolysis.

2. (original) The photocatalytically-activated self-cleaning article of claim 1 wherein the photocatalytically-activated self-cleaning coating comprises a metal oxide selected from the group consisting of titanium oxides, iron oxides, silver oxides, copper oxides, tungsten oxides, aluminum oxides, silicon oxides, zinc stannates, molybdenum oxides, zinc oxides, strontium titanate and mixtures thereof.

3. (original) The photocatalytically-activated self-cleaning article of claim 2 wherein the photocatalytically-activated self-cleaning coating comprises titanium dioxide selected from the group consisting of anatase titanium dioxide, rutile titanium dioxide, brookite titanium dioxide and mixtures thereof.

4. (previously presented) The photocatalytically-activated self-cleaning article of claim 1 wherein said photocatalytically-activated self-cleaning coating is less than or equal to 200 Angstroms thick.

5. (previously presented) The photocatalytically-activated self-cleaning article of claim 1 wherein said photocatalytically-activated self-cleaning coating is less than or equal to 400 Angstroms thick.

6. (previously presented) The photocatalytically-activated self-cleaning article of claim 1 wherein said photocatalytically-activated self-cleaning coating is less than or equal to 500 Angstroms thick.

7. (original) The photocatalytically-activated self-cleaning article of claim 1 wherein said photocatalytically-activated self-cleaning coating has a photocatalytic reaction rate of at least  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

8. (original) The photocatalytically-activated self-cleaning article of claim 7 wherein said photocatalytic reaction rate is determined as the rate of removal of a stearic acid test film in the range of 100 to 200 Angstrom thick deposited over said photocatalytically-activated self-cleaning coating wherein said photocatalytic reaction rate is quantitatively determined as the slope of a curve formed by a plotting of a plurality of Fourier Transform Infrared Spectrophotometer measurements of the integrated intensity of carbon-hydrogen stretching vibrational

absorption bands of the stearic acid test film versus an accumulated time of exposure of said photocatalytically-activated self-cleaning coating to ultraviolet radiation of a frequency within the range of about 300 to 400 nanometers provided by an ultraviolet radiation source positioned over said photocatalytically-activated self-cleaning coating and having an intensity of about 20 watts per square meter as measured at the surface of the photocatalytically-activated self-cleaning coating.

9. (original) The photocatalytically-activated self-cleaning article of claim 8 wherein said ultraviolet radiation source is selected from the group consisting of a black light source and a UVA-340 light source.

10. (original) The photocatalytically-activated self-cleaning article of claim 1 wherein the photocatalytically-activated self-cleaning coating is deposited directly over the substrate.

11. (original) The photocatalytically-activated self-cleaning article of claim 1 further comprising at least one layer interposed between said photocatalytically-activated self-cleaning coating and the substrate.

12. (original) The photocatalytically-activated self-cleaning article of claim 1 wherein said photocatalytically-activated self-cleaning coating comprises one layer of a multilayer stack of coatings deposited over the substrate and wherein the

photocatalytically-activated self-cleaning coating is the uppermost layer of said multilayer stack.

13. (currently amended) A photocatalytically-activated self-cleaning article of manufacture comprising:

\_\_\_\_\_ a substrate having at least one surface; and  
\_\_\_\_\_ a photocatalytically-activated self-cleaning coating deposited over the surface of the substrate at a thickness of less than 1,000 Angstroms by a process selected from the group consisting of chemical vapor deposition, magnetron sputtered vacuum deposition and spray pyrolysis. ~~The photocatalytically-activated self-cleaning article of claim 1~~ wherein said photocatalytically-activated self-cleaning coating comprises one layer of a multilayer stack of coatings deposited over the substrate wherein said photocatalytically-activated self-cleaning coating is a layer other than the uppermost layer of said multilayer stack.

14. (original) The photocatalytically-activated self-cleaning article of claim 1 further comprising a sodium ion diffusion barrier layer disposed between the substrate and the photocatalytically-activated self-cleaning coating to inhibit migration of sodium ions from said substrate to said photocatalytically-activated self-cleaning coating.

15. (original) The photocatalytically-activated self-cleaning article of claim 14 wherein the sodium ion diffusion barrier layer is deposited over the substrate by a

process selected from the group consisting of chemical vapor deposition, magnetron sputtered vacuum deposition and spray pyrolysis.

16. (original) The photocatalytically-activated self-cleaning article of claim 14 wherein the sodium ion diffusion barrier layer is selected from the group consisting a crystalline metal oxide, an amorphous metal oxide and mixtures thereof.

17. (original) The photocatalytically-activated self-cleaning article of claim 16 wherein the sodium ion diffusion barrier layer is selected from the group consisting of tin oxides, silicon oxides, titanium oxides, zirconium oxides, fluorine-doped tin oxides, aluminum oxides, magnesium oxides, zinc oxides, cobalt oxides, chromium oxides, magnesium oxides, iron oxides and mixtures thereof.

18. (original) The photocatalytically-activated self-cleaning article of claim 17 wherein the sodium ion diffusion barrier layer is at least about 250 Angstroms thick.

19. (original) The photocatalytically-activated self-cleaning article of claim 17 wherein the sodium ion diffusion barrier layer is at least about 400 Angstroms thick.

20. (original) The photocatalytically-activated self-cleaning article of claim 17 wherein the sodium ion diffusion barrier layer is at least about 500 Angstroms thick.

21. (original) The photocatalytically-activated self-cleaning article of claim 1 wherein the substrate is selected from the group consisting of glass, plastic, metal, enamel and mixtures thereof.

22. (original) The photocatalytically-activated self-cleaning article of claim 1 wherein said substrate is a glass substrate having a first major surface and an opposite major surface defined as a second major surface, the first major surface having a thin layer of a tin oxide diffused therein characteristic of forming a glass ribbon over a molten tin bath, at least one of the major surfaces having said photocatalytically-activated self-cleaning metal oxide coating deposited thereon.

23. (original) The photocatalytically-activated self-cleaning article of claim 22 wherein the photocatalytically-activated self-cleaning coating further comprises a metal oxide selected from the group consisting of titanium oxides, iron oxides, silver oxides, copper oxides, tungsten oxides, aluminum oxides, silicon oxides, zinc stannates, molybdenum oxides, zinc oxides, strontium titanate and mixtures thereof.

24. (original) The photocatalytically-activated self-cleaning article of claim 23 further comprising a sodium ion diffusion barrier layer disposed between the substrate and the photocatalytically-activated self-cleaning coating.

25. (original) The photocatalytically-activated self-cleaning article of claim 24 wherein the sodium ion diffusion barrier layer is selected from the group consisting of tin oxides, silicon oxides, titanium oxides, zirconium oxides, fluorine-doped tin oxides, aluminum oxides, magnesium oxides, zinc oxides, cobalt oxides, chromium oxides, magnesium oxides, iron oxides and mixtures thereof.

26. (previously presented) The photocatalytically-activated self-cleaning article of claim 22 wherein the photocatalytically-activated self-cleaning metal oxide coating is deposited on the first major surface of the glass substrate and the glass substrate is selected from the group consisting of a glass sheet and a continuous float glass ribbon.

27-40. (canceled)

41. (allowed) A photocatalytically active coated article comprising:

a glass substrate having an air side major surface having sodium ions therein and an opposite major surface having tin diffused therein defined as a tin side major surface; and

a coating over the air side major surface, said coating comprising a photocatalytically-active titanium dioxide layer having a first surface and an opposite surface defined as a second surface with the second surface adjacent the air side major surface of the glass substrate and the second surface of the coating having sodium ions diffused therein from the air side major surface of the

glass substrate, wherein the photocatalytically-active titanium dioxide layer comprises a combination of anatase phase and amorphous phase of titanium dioxide and said layer has a thickness ranging from about 100 to about 1000 Angstroms.

42. (allowed) A photocatalytically active coated article comprising:

a glass substrate having an air side major surface and an opposite major surface having tin therein defined as a tin side major surface; and

a coating over the air side major surface, said coating comprising a photocatalytically-active titanium dioxide layer having a first surface and an opposite surface defined as a second surface with the second surface adjacent the air side major surface of the glass substrate, wherein

(a) the photocatalytically-active titanium dioxide layer comprises a combination of anatase phase and an amorphous phase of titanium dioxide,

(b) said layer has a thickness ranging from about 100 to about 1000 Angstrom,

(c) said tin side major surface has tin diffused therein characteristic of glass formed by pulling molten glass in the form of a glass ribbon across a molten tin bath while cooling the glass ribbon,

(d) said photocatalytically-active titanium dioxide layer was deposited by chemical vapor deposition in the tin bath and this coated glass is exposed to ultraviolet radiation, and



(e) said photocatalytically active titanium dioxide layer has a photocatalytically active self-cleaning reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

43. (allowed) A coated article according to claim 42 wherein the photocatalytically-active self-cleaning reaction rate is at least about  $9.95 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

44. (allowed) A coated article according to claim 42, wherein the glass ribbon is at a temperature of at least about  $538^{\circ} \text{ C}$ .

45. (allowed) A coated article according to claim 42, wherein the glass ribbon is at a temperature of at least about  $600^{\circ} \text{ C}$ .

46. (allowed) A coated article according to claim 42, wherein the photocatalytically-active titanium dioxide layer is activated by exposure to ultraviolet radiation.

47. (allowed) A coated article according to claim 42, wherein the majority of the crystalline phase is anatase.

48. (allowed) A coated article according to claim 42 wherein the second surface of the titanium dioxide layer is directly on and in contact with the air side major surface of the glass substrate.

49. (allowed) A coated article according to claim 42 wherein the phases of the titanium dioxide layer optionally include rutile, and brookite crystalline forms of titanium dioxide.

50. (allowed) A coated article according to claim 42, further comprising a sodium ion diffusion barrier layer between the air side major surface of the glass substrate and the photocatalytically-active titanium dioxide layer, wherein the barrier layer has a thickness of at least about 100 Angstroms.

51. (allowed) A coated article according to claim 50 wherein the photocatalytically-active titanium dioxide layer has a thickness in the range of about 100 to about 2500 Angstroms.

52. (allowed) A coated article according to claim 50, wherein the photocatalytically-active titanium dioxide layer has a thickness in the range of from about 100 to about 1000 Angstroms.

53. (allowed) A coated article according to claim 50, wherein the photocatalytically-active titanium dioxide layer has a thickness in the range of from about 100 to about 500 Angstroms.

54. (allowed) A coated article according to claim 50, wherein the photocatalytically-active titanium dioxide layer has a thickness in the range of from about 100 to about 400 Angstroms.

55. (allowed) A coated article according to claim 50, wherein the photocatalytically-active titanium dioxide layer has a thickness in the range of from about 100 to about 200 Angstroms.

56. (allowed) A coated article according to claim 50, wherein the sodium ion diffusion barrier layer comprises at least one of amorphous and crystalline phase metal oxides selected from cobalt oxides, chromium oxides, iron oxides, tin oxides, titanium oxides, zirconium oxides, fluorine-doped tin oxides, aluminum oxides, magnesium oxides, zinc oxides, and super-oxides and sub-oxides of any of the foregoing.

57. (allowed) A coated article according to claim 50, wherein the sodium ion diffusion barrier layer comprises at least one metal oxide selected from magnesium oxides, aluminum oxides, zinc oxides, tin oxides, and super-oxides and sub-oxides of any of the foregoing.

58. (allowed) A coated article according to claim 50, wherein the sodium ion diffusion barrier layer comprising silicon oxide and has a thickness of at least about 100 Angstroms.

59. (allowed) A coated article according to claim 50 wherein the glass substrate is an annealed glass substrate.

60. (allowed) A coated article according to claim 42 wherein the titanium dioxide layer is formed on a float ribbon at a temperature ranging from about 538° to less than about 800° C.

61. (allowed) A coated article according to claim 42, wherein the titanium dioxide layer is physically durable.

62. (allowed) A coated article according to claim 42, wherein the titanium dioxide layer is resistant to chemical attack.

63. (allowed) A coated article according to claim 42, wherein the photocatalytically-active titanium dioxide layer is capable of having a photocatalytically-activated self-cleaning reaction rate of at least about  $5 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

64. (allowed) A coated article according to claim 42, wherein the photocatalytically-active titanium dioxide layer is capable of having a photocatalytically-activated self-cleaning reaction rate of at least about  $7.79 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

65. (allowed) A coated article according to claim 42, wherein the photocatalytically-active titanium dioxide layer is capable of having a photocatalytically-activated self-cleaning reaction rate of at least about  $12.29 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

66. (canceled)

67. (allowed) A coated glass according to claim 77, wherein the photocatalytically-active titanium dioxide layer is deposited at a temperature ranging from  $554^{\circ}$  to less than about  $800^{\circ}\text{C}$  ( $1029^{\circ}$  to  $1472^{\circ}\text{F}$ ).

68. (allowed) A photocatalytically-activatable self-cleaning article of manufacture comprising:

a glass substrate having a first major surface and an opposite major surface defined as a second major surface, the first major surface having tin diffused therein characteristic of being formed by pulling molten glass in the form of a glass ribbon across a molten tin bath while cooling the glass ribbon, and

a photocatalytically-activatable self-cleaning metal oxide coating having a thickness of less than 1,000 Angstroms over the second major surface capable of having a photocatalytically-activated self-cleaning reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ , where the metal oxide coating was deposited by chemical vapor deposition at a temperature in the range of at least  $400\text{-}800^{\circ}\text{C}$ .

69. (canceled)

70. (allowed) The photocatalytically-activatable self-cleaning article of claim 68 wherein the photocatalytically-activatable coating has a crystalline phase characteristic of chemical vapor deposition of the metal oxide over the second major surface in a molten tin bath where the first major surface is in contact with said tin bath.

71. (allowed) The photocatalytically-activatable self-cleaning article of claim 68 further comprising at least one layer interposed between the photocatalytically-activatable self-cleaning coating and the substrate.

72. (allowed) The photocatalytically-activatable self-cleaning article of claim 71, wherein the at least one layer has at least one oxide chosen from crystalline metal oxides, amorphous metal oxides, crystalline silicon oxides and amorphous silicon oxides.

73. (allowed) The photocatalytically-activatable self-cleaning article of claim 71, wherein at least one layer is chosen from iron oxides, silver oxides, copper oxides, tungsten oxides, zinc oxides, zinc/tin oxides, strontium titanate, and titanium oxides chosen from anatase, rutile, and brookite crystalline forms of titanium dioxide.

74. (allowed) The photocatalytically-activatable self-cleaning article of claim 68 wherein the photocatalytically-activatable coating has an anatase titanium oxide phase characteristic of chemical vapor deposition over the second major surface in a molten tin bath where the first major surface is in contact with said tin bath and wherein the article has at least one layer interposed between the photocatalytically-activatable self-cleaning coating and the substrate where the at least one layer comprises at least one oxide chosen from amorphous and crystalline metal oxides, and silicone oxides.

75. (allowed) The photocatalytically-activatable self-cleaning article of claim 74 wherein the metal oxides are chosen from cobalt oxides, chromium oxides, iron oxides, tin oxides, titanium oxides, zirconium oxides, fluorine-doped tin oxides, aluminum oxides, magnesium oxides, and zinc oxides.

76. (allowed) A photocatalytically-activatable coated glass comprising:  
a glass substrate having an air side major surface and a tin side major surface having been formed in a tin bath of a float glass process;  
a coating over the air side major surface, said coating comprising a photocatalytically-activatable titanium dioxide layer having a first surface and a second surface with the second surface adjacent the air side major surface,  
wherein the photocatalytically-activatable titanium dioxide layer

comprises anatase titanium dioxide and said layer has a thickness ranging from about 100 to about 1000 Angstroms;

and wherein the coated glass comprises an interlayer between the photocatalytically-activatable layer second surface and the air side major surface of the substrate, said interlayer comprising amorphous silicon oxide.

77. (allowed). A photocatalytically-active coated glass comprising:

a glass substrate having an air side major surface and a tin side major surface having been formed in a tin bath of a float glass process;

a coating over the air side major surface of the substrate, said coating comprising a photocatalytically-active titanium dioxide layer having a first surface and a second surface with the second surface adjacent the air side major surface wherein the photocatalytically-active titanium dioxide layer comprises anatase titanium dioxide having a thickness of less than 1000 Angstroms, and

an interlayer between the second surface of the photocatalytically-active layer and the air side major surface of the substrate, said interlayer comprising amorphous silicon oxide,

wherein said tin side major surface has tin diffused therein characteristic of being formed from a glass ribbon floated in a molten tin bath;

wherein said photocatalytically-active titanium dioxide layer was deposited by chemical vapor deposition in said tin bath and exposed to ultraviolet radiation, and



further wherein said photocatalytically-active titanium dioxide layer has a photocatalytically-active self-cleaning reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

78. (allowed) A photocatalytically-active coated glass comprising:

a glass substrate having an air side major surface and a tin side major surface, the tin side major surface having tin oxide characteristic of glass formed by pulling molten glass in the form of a glass ribbon across a molten tin bath while cooling the glass ribbon; and

a coating over the air side major surface, said coating comprising a photocatalytically-active titanium dioxide layer having a first surface and a second surface with the second surface adjacent the air side major surface, wherein said layer

(a) has a thickness ranging from about 100 to about 1000 Angstroms,

(b) was deposited by chemical vapor deposition in said tin bath and exposed to ultraviolet radiation, and

(c) has a photocatalytically-active self-cleaning reaction rate of at least  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

79. (allowed) The article of Claim 77 wherein the photocatalytically-active self-cleaning reaction rate is at least about  $9.95 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

80. (allowed) A photocatalytically active coated glass comprising:

a glass substrate having an air side major surface and a tin side major surface, the tin side major surface having tin oxide therein characteristic of glass formed by pulling molten glass in the form of a glass ribbon across a molten tin while cooling the glass ribbon;

a sodium ion diffusion barrier layer over said air side major surface, and  
a coating over the sodium ion diffusion barrier layer, said coating comprising a photocatalytically-active titanium dioxide layer having a first surface and a second surface with the second surface adjacent the sodium ion diffusion barrier layer, wherein the photocatalytically active titanium dioxide layer has a thickness ranging from about 100 to about 1000 Angstroms, was deposited by chemical vapor deposition in said tin bath, and has a photocatalytically active self-cleaning reaction rate of at least about  $9.95 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

81. (allowed) The coated glass of claim 80 wherein the photocatalytically-active titanium dioxide layer comprises a combination of an anatase phase and an amorphous phase of titanium dioxide.

82. (canceled)